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(54) LIGHTWEIGHT GLASS FIBRE REINFORCED POLYESTER ARTICLE AND METHOD OF MAKING THE SAME

(71) We, FREEMAN CHEMICAL CORPORATION, a corporation organised under the laws of the State of Delaware, U.S.A., with principal offices at 222 East Main Street, Port Washington, Wisconsin 53074, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention concerns glass fibre articles utilizing unsaturated polyester resin syrup. Unsaturated polyester resin syrup and chopped glass fibres have been combined to produce glass fibre reinforced plastic articles. See "Polyesters and Their Applications", Bjorksten et al, Reinhold Publishing Corporation, 1956. The resulting articles have a high strength-to-weight ratio, good resiliency, electrical properties, resistance to corrosion, moldability. Such materials have been employed in aircraft components, boats, automobile components, light transmissive building sheeting, snowmobiles, gold carts, chairs, piping, tanks, window surrounds, bathroom vanities, bathtubs and shower stalls, building panels.

One type of product, known as a lay-up or spray-up article, is obtained by spraying the unsaturated polyester resin syrup along with appropriate free radical initiators, accelerators, surfactants, inhibitors, pigments, dyes or fillers against a stream of chopped glass fibres whereby the fibres are wetted and collected on a substrate. Customarily the wetted glass fibres are thereupon rolled or tamped to embed the loose ends of the glass fibres and eliminate gas pockets. The wetted fibres are retained in engagement with the substrate until the resinous components cure. Customarily the free radical initiator and the promoter are selected so that the curing will commence at room temperatures.

The curing is exothermic and causes a general increase in the temperature of the article. Complete cures in spray-up or lay-up operations normally require about one to four hours before the glass fibre reinforced article can be separated from the substrate and withdrawn as a product.

It is an object of the present invention to provide glass fibre reinforced unsaturated polyester resin articles which are without significant sacrifice in the strength of the product as compared with known articles but which will have a substantially lowered density which permits production of useful articles with less materials.

According to the present invention there is provided an article reinforced with chopped glass fibre containing 15 to 50% by weight of randomly oriented glass fibres confined in a continuous mass of cellular polymerised unsaturated polyester resin syrup containing 75 to 55% by weight of unsaturated polyester and 25 to 45% by weight of monomer, the cells of said mass containing a gas having a greater nitrogen content than the atmosphere, said article having a density of 15 to 60 pounds per cubic foot.

According to a further feature of the present invention there is provided a method of producing an article reinforced with chopped glass fibre which comprises wetting a stream of chopped glass fibres with a mixture comprising an unsaturated polyester resin syrup containing 75 to 55% by weight of unsaturated polyester and 25 to 45% by weight of monomer, an alpha hydroxy azo blowing agent, a polymerisation initiator and a metal salt accelerator, said mixture containing 0.5 to 5.0 parts by weight of said blowing agent for each 100 parts by weight of said resin syrup, collecting said wetted glass fibres as a coating on a substrate and allowing said coating to polymerise to provide a glass fibre reinforced article having

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a density less than 75% of the density of a corresponding article which would be obtained in the absence of said blowing agent.

5 In one method according to the invention, the mixture for wetting the glass fibres is formed by delivery to a mixing zone of a first stream containing the liquid resin syrup, and a second stream containing the blowing agent, mixing the two streams in the mixing zone and immediately spraying the resulting mixture onto a stream of chopped glass fibres.

10 In one alternative method there is first formed a spray containing resin syrup and a second spray containing blowing agent, one spray being impinged on the other to form a combined spray, said combined spray being directed against a descending stream of chopped glass fibres.

20 The wetting mixture for the glass fibres will in general include also surfactants, polymerisation inhibitors and fillers.

25 Cellular plastic materials have been defined as "a plastic, the apparent density of which is decreased substantially by the presence of numerous cells disposed throughout its mass". The foaming of the present process arises from the nitrogen gas which is developed from the alpha hydroxy azo blowing agent. The expanding nitrogen gas creates the cells and is confined therein in concentrations which exceed the atmospheric nitrogen concentration.

30 In contrast with polyurethane foams the polyester foams of the present invention are essentially free of urethane linkages and allophanate linkages.

35 Figure 1 is a schematic illustration of apparatus useful in practicing a preferred embodiment of the present invention.

40 Figure 2 is a fragmentary schematic illustration of equipment for practicing an alternative embodiment of the present invention.

45 The three essential ingredients of the present invention are chopped glass fibres, unsaturated polyester resin syrups and alpha hydroxy azo blowing agents.

Unsaturated Polyester Resin Syrup

50 The unsaturated polyester resin syrup is a solution of an unsaturated polyester resin in a copolymerizable monomer which is usually styrene but may be other ethylenically unsaturated monomers such as vinyl toluene, divinyl benzene, acrylic acid, methacrylic acid, alkyl acrylates and methacrylates, ortho - chlorostyrene, alpha - methylstyrene, ethylene glycol dimethacrylate. The unsaturated polyester resin is formed by polyesterification of polyol and polycarboxylic acid or polycarboxylic acid anhydride at least a portion of which contains ethylenic unsaturation.

Typical polyols include glycols such as

ethylene glycol, propylene glycol, butylene glycol, neopentyl glycol, diethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol and the like. The polycarboxylic acid or anhydride may include materials which do not possess ethylenic unsaturation such as phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, adipic acid, succinic acid, glutaric acid, malonic acid, pimelic acid, sorbic acid, halogenated dibasic acids. Typical unsaturated dicarboxylic acids or anhydrides include maleic acid, maleic anhydride, fumaric acid, endomethylene - tetrahydrophthalic acid or anhydride, itaconic acid and the like. Typically the unsaturated polyester resin is prepared by polyesterification of an excess of polyol with polycarboxylic acid. Typically at least 40 mol percent of the polycarboxylic acid is ethylenically unsaturated polycarboxylic acid. The acid and polyol are cooked in the presence of a polyesterification catalyst until the polyesterification is essentially completed as indicated by the acid number of the resulting product being reduced to 30 or less. The unsaturated polyester resin syrup contains about 1 part by weight of copolymerizable monomer for every 1 to 10 parts by weight of the unsaturated polyester resin.

As stated the unsaturated polyester resin syrup contains 25 to 45 weight percent monomer and 75 to 55 weight percent unsaturated polyester. In connection with the present invention, when the monomer content is below about 25 percent, the resulting syrup is difficult to spray. When the monomer content exceeds 45 weight percent the monomer tends to separate out as a distinct phase from the foaming, ungelled resin.

Polymerisation Initiator

105 Preferably the polymerisation initiator employed is a high temperature initiator and suitably provided from in an amount of from 0.2 to 2 percent by weight of the unsaturated polyester resin syrup. Useful initiators include tertiary butyl perbenzoate ditertiary butyl perbenzoate, cumene hydroperoxide, methylethylketone peroxide and tertiary butyl hydroperoxide. These initiators are ineffective at room temperature but become effective when the temperature is increased, particularly in the presence of metal salt promoters.

120 The polymerisation initiator is preferably incorporated in the unsaturated polyester resin syrup. Peroxy type initiators, if employed, are used in the unsaturated polyester resin syrup. Other types of initiators may be combined with the alpha hydroxy azo blowing agent or with the unsaturated polyester resin syrup.

125 Metal Salt Accelerators, i.e. Promoters
The present compositions contain metal

salt accelerators preferably in amounts from 1 to 100 parts by weight per million (p.p.m.) of the weight of the unsaturated polyester resin syrup. A preferred promoter is copper naphthenate solution although cobalt salts, vanadium salts, manganese salts, calcium salts, magnesium salts can also be employed.

Surfactants

If it is desired to produce a foamed product having relatively uniform foam cell sizes, a small quantity of a silicone surfactant is employed in the amount of 0.1 to 2.5 weight percent of the unsaturated polyester resin syrup.

Inhibitors

Customarily unsaturated polyester resin syrups are provided with polymerization inhibitors to forestall unintended premature gelation.

Fillers

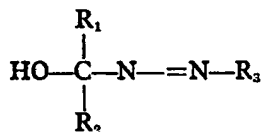
The unsaturated polyester resin syrup may be filled with inert materials such as pigments, dyes, aluminum oxide trihydrate, silica, limestone, ground glass, clays, mica and thixotropic additives such as silica aerogel.

Where thixotropic additives are employed they are used in quantities ranging from about 1/2 to about 3 percent by weight of the unsaturated polyester resin syrup. The other inert fillers may be employed up to about an equal weight of the unsaturated polyester resin syrup.

A particularly preferred inorganic filler is powdered aluminum oxide trihydrate from about 70 to 110 percent of the weight of the unsaturated polyester resin syrup. At concentrations above about 110 percent by weight aluminum oxide trihydrate, the resulting mixture cannot be sprayed. At concentrations below about 70 percent by weight aluminum oxide trihydrate, no substantial benefit is observed. However when the aluminum oxide trihydrate is employed from about 70 to 110 percent by weight of the unsaturated polyester resin syrup, the resulting article exhibits outstanding flame spread ratings and smoke index ratings.

The Alpha Hydroxy Azo Blowing Agent

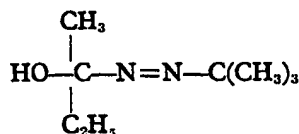
Suitable alpha hydroxy azo blowing agents have the following general formula:



wherein R_1 and R_2 are lower alkyl groups having from 1 to 4 carbon atoms and R_3 is a tertiary alkyl group having 4 to 8

carbon atoms or an aromatic substituted tertiary alkyl group having 9 to 12 carbon atoms. Examples of R_3 substituent are the tertiary-butyl radical and the alpha-cumyl radical.

A preferred alpha hydroxy azo blowing agent is identified as blowing agent I having the following formula:



The azo blowing agent may be employed full strength or it may be diluted with inert solvents which will not impede the polymerization of the polyester resin syrup. Such solvents include mineral oil and styrene for example.

Glass Fibres

The glass fibres employed in the present reinforced articles are normally the type which are conventionally used in glass fibre reinforced articles, that is, chopped glass, roving with an average length of about 3/8 inch to about 4 inches although lengths ranging from 1/2 inch to 1 inch are normally preferred. Commercial glass roving is usually coated with a silane sizing to improve bond with the resins. The glass fibres normally constitute from about 5 to 30 weight percent of the product.

The Present Process

As shown in Figure 1, a tank 10 is supplied with an unsaturated polyester resin syrup containing suitable quantities of free radical initiator, promoter, surfactant, and, if desired, inert fillers. A tank 11 contains the alpha hydroxy azo blowing agent in liquid form.

A spool 12 contains glass fibre rovings of the type customarily employed in producing glass fibre reinforced plastic articles.

Unsaturated polyester resin syrup from the tank 10 is delivered through a tube 13 to a spray gun 14. The alpha hydroxy azo blowing agent is delivered from the tank 11 through a tube 15 to the spray gun 14. A supply of pressurized air is delivered through the tube 16 to the spray gun 14. Within the spray gun 14 there is a mixing chamber where the unsaturated polyester resin syrup and the alpha hydroxy azo blowing agent are mixed and formed into a spray 17 by the atomization from the compressed air in the spray gun 14.

Concurrently the glass fibre roving 18 is drawn from the spool 12 and chopped in a chopper 19 to form a descending cloud 20 of chopped glass fibres which impinge the spray 17 and thereby become wetted with

the spray mixture. The wetted fibres 17 fall onto a substrate 21 and are collected as a coating 22. The exposed surface 23 of the substrate 21 is coated with a suitable mold release agent to facilitate subsequent separation of the coating 22 from the substrate 21. Alternatively the substrate 21 may be a final product which will contain the coating 22 in its completed form. An example is where the substrate 21 is a premolded sheet of acrylic resin shaped into the form of a bathtub. The coating 22, as deposited, contains randomly oriented glass fibres and objectionable air pockets. Accordingly, it is preferred that the coating 22 be rolled and/or tamped to embed any projecting glass fibres and to minimize the unintended porosity resulting from unwanted air pockets. The rolling and tamping should be carried out promptly inasmuch as the mixture of unsaturated polyester resin syrup and alpha hydroxy azo blowing agent commences gelation almost immediately upon mixing. The coating 22, following rolling and/or tamping, should be allowed to remain quiescent for a suitable time to allow the coating to develop an exotherm, to complete cure and commence cooling.

Example 1

A commercially available unsaturated polyester resin is fabricated from 105 mol parts by weight propylene glycol, 50 mol parts isophthalic acid and 50 mol parts by weight maleic anhydride. The three ingredients are cooked to a final acid value between 17 and 25, measured at 60 percent by weight solids content in methyl 'Cellosolve' [Cellosolve is a Registered Trade Mark] solvent. 73 parts by weight of the described unsaturated polyester resin is combined with 27 parts by weight of styrene to produce an unsaturated polyester resin syrup having an acid value of 27 to 33.

The unsaturated polyester resin syrup was combined with 0.5 weight percent tertiary butyl perbenzoate as a free radical initiator, 1 percent by weight silicone fluid as a surfactant, 4-1/2 parts per million by weight of copper naphthenate as an accelerator. No filler was employed in this example. The chopped glass roving was a type known in the trade as 60-end roving chopped into lengths of 1-1/2 to 3 inches.

The alpha hydroxy azo blowing agent I was employed at a flow rate of 1 percent by weight of the unsaturated polyester resin flow rate. Both the unsaturated polyester resin and the alpha hydroxy azo blowing agent I were introduced into a spray gun combined with a glass roving chopper. The chopped glass fibres, wetted with the combined spray, were applied against a drum lid mould which was previously coated with a mould release agent. The spray was applied in three passes

over the surface. The coated drum lid was rolled with a glass compacter roller and allowed to rise freely at room temperature. The article was demolded from the drum lid after about 15 minutes. The article had a flexural strength of 4100 psi, a flexural modulus of 0.26×10^9 psi, a tensile strength of 2900 psi, a tensile modulus of 0.217×10^9 psi, a density of 26 pounds per cubic foot and a closed cell content of about 92 percent. The article contained 26 percent by weight glass fibres. The starting thickness of the article after compacter rolling was 0.125 inch. After curing the final article thickness was 0.432 inch.

Example 2

For purposes of comparison conventional article was prepared from the unsaturated polyester resin syrup described in Example 1 combined with an equal weight of powdered aluminum oxide trihydrate. The 50-50 mixture of aluminum oxide trihydrate and unsaturated polyester resin syrup was sprayed with chopped glass fibres to produce an article having a final density after cure of about 90 pounds per cubic foot.

Example 3

The filled unsaturated polyester resin syrup of Example 2 including an equal weight of aluminum oxide trihydrate was combined in a spray gun as described in Example 1 with 1 percent by weight of alpha hydroxy azo blowing agent type I. Chopped glass fibres wetted with the combined spray produced an article having a density of about 45 pounds per cubic foot. This article was subjected to combustion tests in an Underwriters' Laboratories test and yielded a smoke index of 182 and a flame spread of 44. The glass content in the panel was 20 percent by weight. The panel had a thickness from about 1/4 inch to about 1/2 inch.

The article of Example 3 had a density (45 p.c.f.) about 50 percent of the density of the Example 2 article (90 p.c.f.).

Example 4

The foamed resinous materials in accordance with the present invention were employed in the construction of a number of boats, one of which will be described. A 21 foot long inboard motor boat hull was prepared from a commercial hull mould which itself was fabricated from reinforced polyester materials. Initially a mould release agent was applied to the surface of the hull mould by wiping with a rag. Thereafter a pigmented gel coat was sprayed over the entire surface and allowed to cure. Thereafter a conventional unsaturated polyester resin and glass fibre spray-up coating was applied over the cured gel coat in an average thickness of about 80 mils. This spray-up

coating was allowed to cure. Thereafter a number of pre-cut wooden reinforcing stringers and cross-pieces were applied against the cured spray-up coating by press fitting.

Thereafter a polyester resin foam and glass fibre coating of this invention was applied to the original spray-up coating to an initial thickness of about 15 mils prior to foaming. After foaming the coating had a thickness of about 40 mils. The foam-glass fibre coating covered the side surfaces of the wooden stringers and cross-pieces and served as a binder for retaining them permanently in position.

After the foamed resin coating had been cured, a further skin coating of unsaturated polyester resin and glass fibres was applied as a spray-up coating in a thickness of about 80 mils. The total thickness of the boat hull was 0.4 to 0.5 inch. The total weight of the boat hull including wooden stringers and cross-pieces was about 400 pounds.

Corresponding boats are made commercially from conventional polyester resin and glass spray-up techniques in two separate spray-up operations having a total thickness of 0.25 to 0.375 inch. A conventional boat hull, if overturned, will sink in water. The boat hull manufactured in accordance with this invention had the same total weight as the conventional boat hull but floated when overturned.

The foamed polyester glass spray-up employed a polyester fabricated from a 50/50 weight percent mixture of isophthalic acid and maleic anhydride esterified with a slight excess of propylene glycol to an acid value of about 18 at 60 percent solids. The polyester is mixed into a syrup containing 40 percent by weight styrene, 0.5 weight percent of a silicone surfactant, 0.7 weight percent tertiary butyl perbenzoate and 6 parts by weight per million of copper naphthenate. This material is combined with 1.75 weight percent (based on the weight of the polyester syrup) of the azo blowing agent I. The chopped glass fibres constitute 18 percent of the weight of the foam layer. Two samples of the foamed glass layer taken at different times showed densities of 23 pounds per cubic foot and 34 pounds per cubic foot.

The foamed polyester-glass fibre coating served to adhere the wooden stringers and wooden cross-pieces firmly to the boat hull surfaces.

General

Inhibitors which are customarily employed with unsaturated polyester syrups are not effective in the presence of alpha hydroxy azo blowing agents. In a typical unsaturated polyester resin syrup, the addition of 1,000 p.p.m. hydroquinone will extend the gel time

about three-fold. Where an alpha hydroxy azo blowing agent is employed, 1,000 p.p.m. hydroquinone extends the gel time by only about 10 percent.

Alternative Method

Referring to Figure 2, an alternative method for making the present spray-up, lay-up articles is illustrated which employs two different spray nozzles identified by the numerals 24, 25. Compressed air from a tube 16A is delivered to both of the nozzles 24, 25. The unsaturated polyester resin syrup is delivered from 10 through a tube 13A to the nozzle 24. The alpha hydroxy azo blowing agent is delivered from 11 through a tube 15A to the spray nozzle 25 whence it emanates as a spray 26. The unsaturated polyester resin syrup is delivered as a spray 27 from the nozzle 24. The two sprays 26, 27 combine to produce a composite spray 28 wherein the alpha hydroxy azo blowing agent is intimately admixed with the unsaturated polyester resin syrup. The combined spray 28 wets a descending cloud 20A of glass fibres to form a coating 22A on the substrate 21A.

Some of the useful products which can be fabricated from the present process include one-piece tub and shower stall units, bathroom vanities, automobile fenders and hoods, cold molded formed shapes such as building window surrounds and cornices, backing for thermoformed acrylic sheeting, snowmobile shrouds, barge covers, building infill panels, mobile homes, liners for railroad boxcars, tote boxes, silo roofs and panels, tanks and the like, boat hulls, surfboards.

WHAT WE CLAIM IS:—

1. An article reinforced with chopped glass fibre containing 15 to 50% by weight of randomly oriented glass fibres confined in a continuous mass of cellular polymerised unsaturated polyester resin syrup containing 75 to 55% by weight of unsaturated polyester and 25 to 45% by weight of monomer, the cells of said mass containing a gas having a greater nitrogen content than the atmosphere, said article having a density of 15 to 60 pounds per cubic foot.

2. An article reinforced with chopped glass fibre according to claim 1 wherein the cellular mass contains 70 to 110% by weight of powdered aluminium oxide trihydrate based upon the weight of said polymerised unsaturated polyester resin in the article.

3. An article reinforced with chopped glass fibre according to claim 1 substantially as herein described.

4. A method of producing an article reinforced with chopped glass fibre as claimed in claim 1 which comprises wetting a stream

of chopped glass fibres with a mixture comprising an unsaturated polyester resin syrup containing 75 to 55% by weight of unsaturated polyester and 25 to 45% by weight of monomer, an alpha hydroxy azo blowing agent, a polymerisation initiator and a metal salt accelerator, said mixture containing 0.5 to 5.0 parts by weight of said blowing agent for each 100 parts by weight of said resin syrup, collecting said wetted glass fibres as a coating on a substrate and allowing said coating to polymerise to provide a glass fibre reinforced article having a density less than 75% of the density of a corresponding article which would be obtained in the absence of said blowing agent.

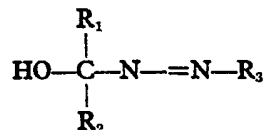
5. A method according to claim 4, wherein the mixture for wetting the glass fibres is formed by delivery to a mixing zone of a first stream containing the liquid resin syrup and a second stream containing the blowing agent, mixing the two streams in the mixing zone and immediately spraying the resulting mixture onto a stream of chopped glass fibres.

6. A method according to claim 4, wherein there is formed a first spray containing resin syrup and a second spray containing blowing agent, one spray being impinged on the other to form a combined spray, said combined spray being directed against a descending stream of chopped glass fibres.

7. A method according to any of claims 4 to 6, wherein the resin syrup includes powdered aluminium oxide trihydrate in an amount sufficient to constitute 70 to 110% by weight of the said resin syrup.

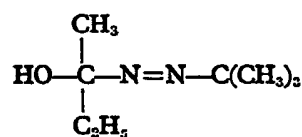
8. A method according to any of claims 4

to 7, wherein the alpha hydroxy azo blowing agent has the formula



wherein R_1 and R_2 are lower alkyl groups having from 1 to 4 carbon atoms and R_3 is a tertiary alkyl group having from 4 to 8 carbon atoms or an aromatic substituted tertiary alkyl group having from 9 to 12 carbon atoms.

9. A method according to claim 8 wherein the alpha hydroxy azo blowing agent has the formula

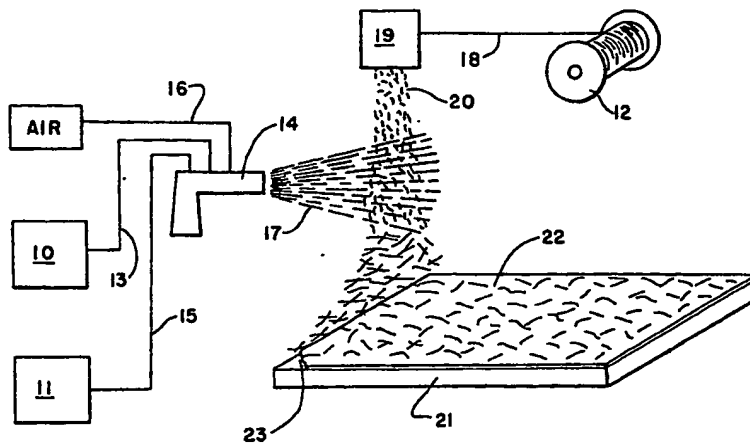
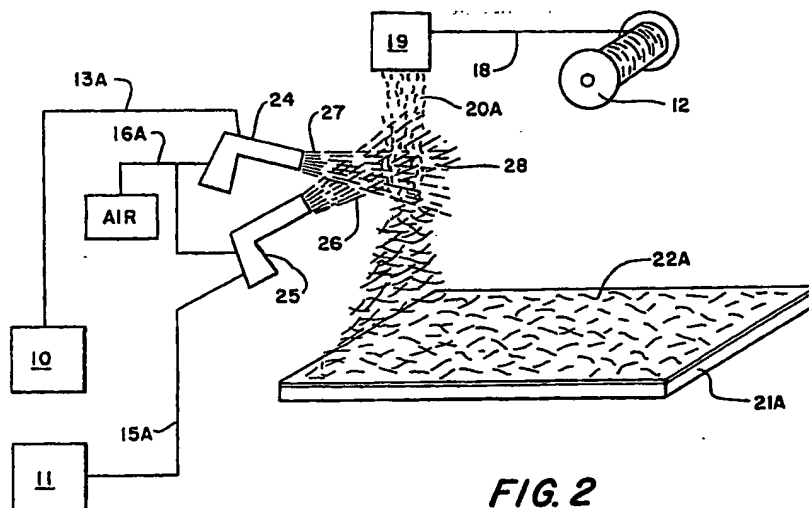


10. A method according to any of the preceding claims 4 to 9, wherein the collected wetted fibres are rolled or tamped to embed loose ends of the glass fibres and eliminate gas pockets.

11. A method of producing an article reinforced with chopped glass fibre according to claim 1, substantially as herein described.

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**FIG. 1****FIG. 2**

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